SUPPORTING INFORMATION

Growth Mechanism and Electronic Structure of Zn_3P_2 on the Ga-rich GaAs(001) Surface

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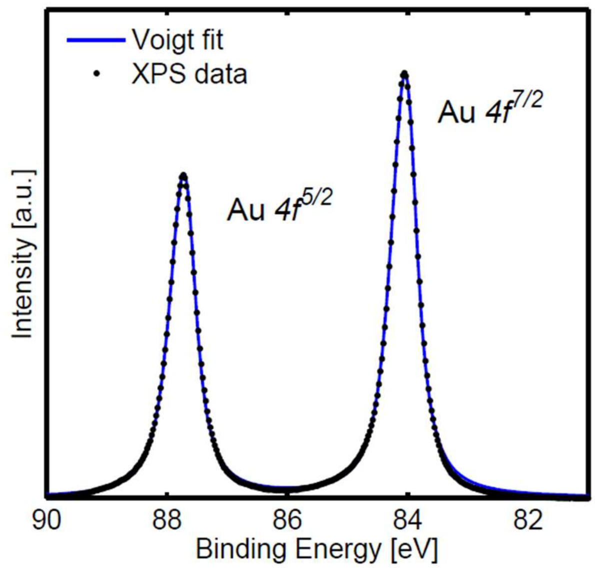

Figure S1. Au 4*f* core-level XPS spectra (black dots) and fitting (blue curve). Au 4*f* core-level XPS spectra were taken for reference from a 100 µm thick gold foil. The foil was cleaned with several cycles of sputtering (5 kV, Ar ion) and annealing at 650 ˚C in the Kratos system (background pressure 2E-9 torr). The pass energy and step size of the analyzer were 20 and 0.025 eV, respectfully. The inherent lifetime broadening of the Au 4*f* core level is known to be 0.317 ± 0.010 eV [1], indicating that the Kratos instrument energy resolution was < 0.20 eV.

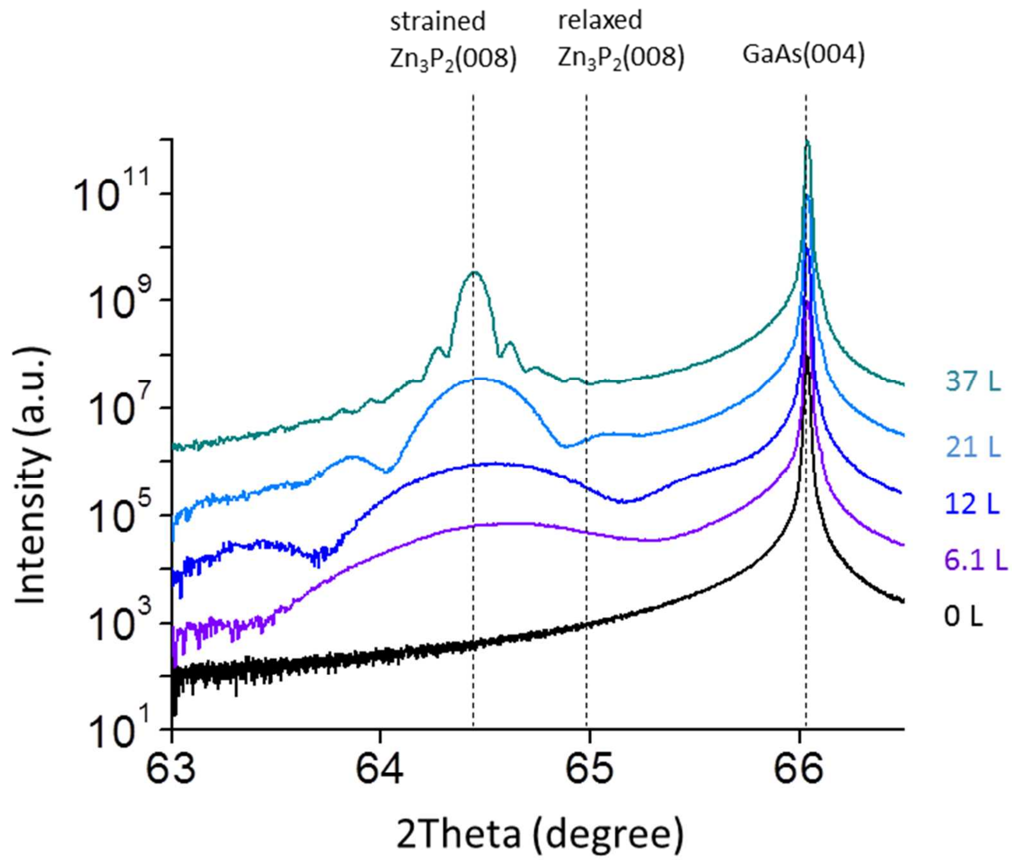

Figure S2. Symmetric HRXRD scans of the Zn_3P_2/GaAs(001) with the Zn_3P_2 deposition amount of 0, 6.1, 12, 21, and 37 L. Vertical dashed lines indicate the diffraction peak positions of pseudomorphic epitaxy Zn_3P_2 (008), crystalline Zn_3P_2 (008), and crystalline GaAs(004), respectively.

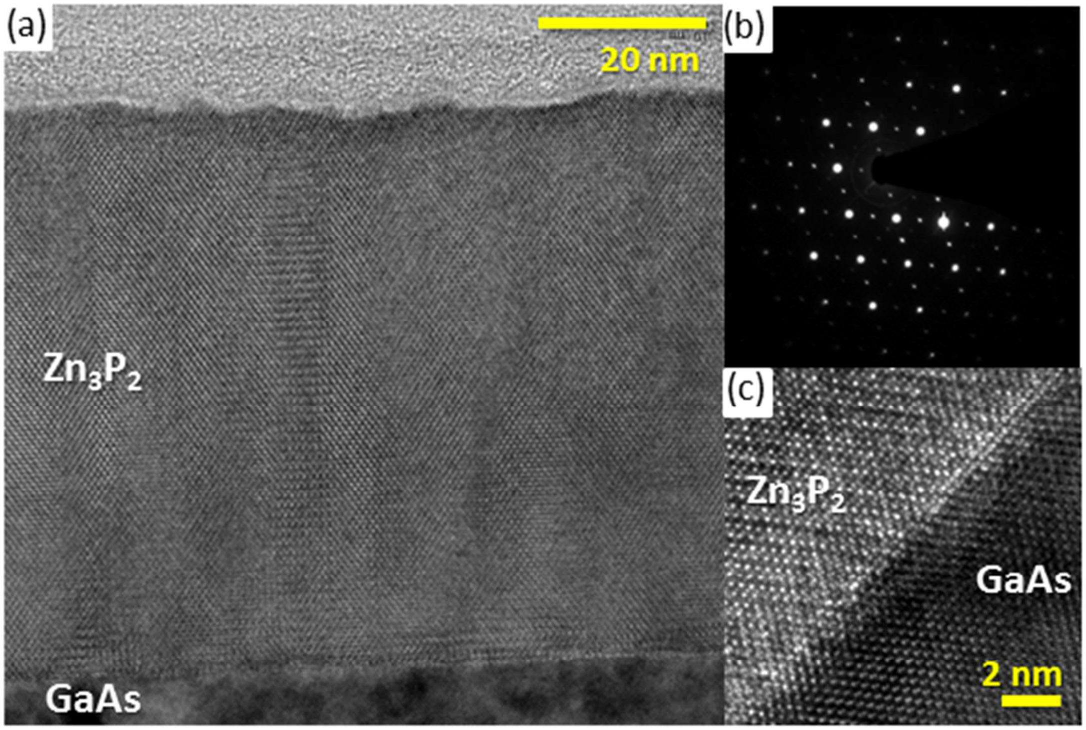

Figure S3. (a), (c) TEM images of the Zn_3P_2/GaAs(001) with the Zn_3P_2 deposition amount of 37L. (b) SAED image of the Zn_3P_2/GaAs(001).

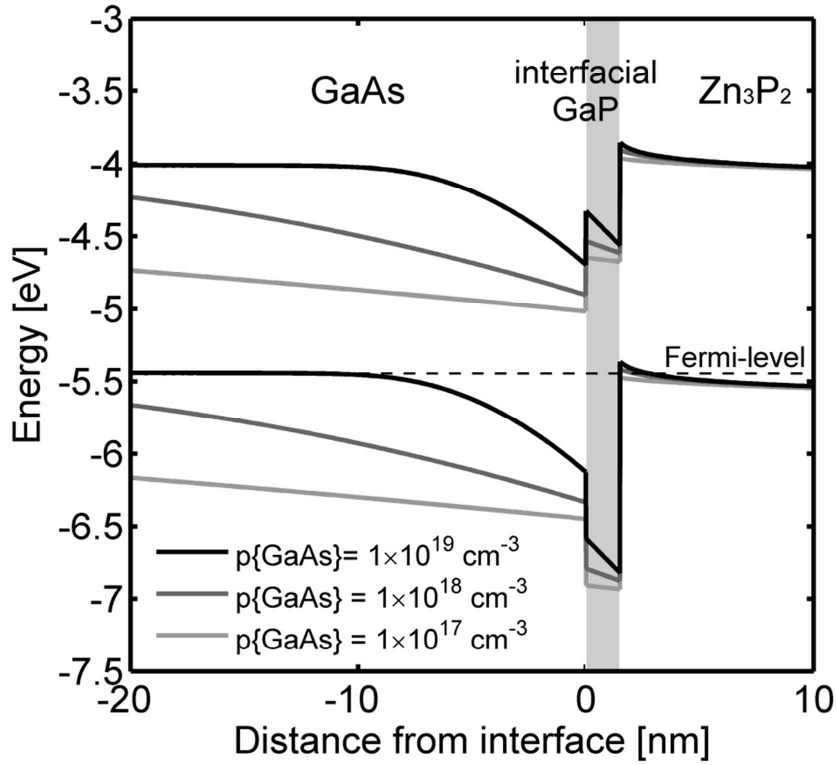

Figure S4. Calculate energy band diagrams of a Zn_3P_2/GaAs(001) heterojunction with a 1.0 nm thick GaP interfacial layer as a function of the GaAs substrate hole concentration. The Zn_3P_2 hole concentration was fixed at 1×10^{16} cm^{-3} and the GaP interfacial layer was treated as intrinsic.

DFT calculation supplement

Surface formation energy of a ternary alloy is defined as,

$$E_{surf} = \frac{1}{A}[E(mnl) - m\mu(Ga) - n\mu(As) - l\mu(P)]$$

A: Area of surface

m, n, and l: Number of Ga, As, and P atoms, respectively

E(mnl): Ab-initio total energy of a surface model including *m* of Ga atoms, *n* of As atoms, and *l* of P atoms

μ(B): Chemical potential of atom B (B = Ga, As, or P)

Change of surface formation energy with respect to a reference structure,

$$\Delta E_{surf} = \frac{1}{A}\left[E(mnl) - E_{ref}(m'\,n'\,l') + \mu(Ga)(m'-m) + \mu(As)(n'-n) + \mu(P)(l'-l)\right]$$

In our system,

1) The number of Ga atoms are maintained ($m' - m = 0$)
2) Anion replacement of As by P maintains total number of As and P ($n + l = n' + l'$)
3) Δμ(P) and Δμ(As) are defined as follows

$$\Delta\mu(P) = \mu(P) - \mu(P^{bulk}),\ (\Delta H_f(GaP) \le \Delta\mu(P) \le 0)$$

$$\Delta\mu(As) = \mu(As) - \mu(As^{bulk}), (\Delta H_f(GaAs) \le \Delta\mu(As) \le 0)$$

By substituting equations in 1) ~ 3) into ΔE_{surf}, we obtain,

$$\Delta E_{surf} = \frac{1}{A}\{E(mnl) - E_{ref}(m'\,n'\,l') +$$

$(l' - l)[\mu(P^{bulk}) - \mu(As^{bulk}) + \Delta\mu(P) - \Delta\mu(As)]\}$

$E_{ref}(m'\ n'\ l')$: Calculated total energy of the GaAs(001)-β2(2×4) surface model including m' of Ga atoms, n' of As atoms, and l' of P atoms

$\mu(P^{bulk}) = -5.27575\ eV$: Calculated chemical potential of P from black phosphorus

$\mu(As^{bulk}) = -4.25974\ eV$: Calculated chemical potential of As from crystalline arsenic

$\Delta H_f(GaP) = -1.086\ eV$: Heat of formation of bulk GaP [2]

$\Delta H_f(GaAs) = -0.847\ eV$: Heat of formation of bulk GaAs [2]

REFERENCE

(1) Kraut, E. A.; Grant, R. W.; Waldrop, J. R.; Kowalczyk, S. P. Semiconductor core-level to valence-band maximum binding-energy differences: Precise determination by x-ray photoelectron spectroscopy. *Phys. Rev. B* **1983,** 28, 1965.

(2) *Landolt-Bornstein Numerical Data and Functional Relationships in Science and Techenology - New Series, Group III: Crystal and Solid State Physics*; Springer-Verlag: Berlin, 1982, 17